

FORM PTO-1390 (Modified) REV 10-95		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE		ATTORNEY'S DOCKET NUMBER AD6516	
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371				U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR 09/462971	
INTERNATIONAL APPLICATION NO. PCT/US98/15229		INTERNATIONAL FILING DATE 23 JULY 1998 (23.07.98)		PRIORITY DATE CLAIMED 25 JULY 1997 (25.07.97)	
TITLE OF INVENTION FLAME RETARDANT POLYOLEFIN COMPOSITIONS					
APPLICANT(S) FOR DO/EO/US GARCIA DURAN, Juan-Antonio et al.					
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information					
<ol style="list-style-type: none"> 1. <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. 371. 2. <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371. 3. <input checked="" type="checkbox"/> This is an express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1). 4. <input checked="" type="checkbox"/> A proper Demand for International Preliminary Examination was made by the 19th month from the earliest claimed priority date. 5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371 (c) (2)) <ol style="list-style-type: none"> a. <input checked="" type="checkbox"/> is transmitted herewith (required only if not transmitted by the International Bureau). b. <input type="checkbox"/> has been transmitted by the International Bureau. c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US). 6. <input type="checkbox"/> A translation of the International Application into English (35 U.S.C. 371(c)(2)). 7. <input checked="" type="checkbox"/> A copy of the International Search Report (PCT/ISA/210). 8. <input type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3)) <ol style="list-style-type: none"> a. <input type="checkbox"/> are transmitted herewith (required only if not transmitted by the International Bureau). b. <input type="checkbox"/> have been transmitted by the International Bureau. c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired. d. <input checked="" type="checkbox"/> have not been made and will not be made. 9. <input type="checkbox"/> A translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)). 10. <input type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)). 11. <input checked="" type="checkbox"/> A copy of the International Preliminary Examination Report (PCT/IPEA/409). 12. <input type="checkbox"/> A translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)). 					
Items 13 to 18 below concern document(s) or information included:					
<ol style="list-style-type: none"> 13. <input type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98. 14. <input type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included. 15. <input type="checkbox"/> A FIRST preliminary amendment. A SECOND or SUBSEQUENT preliminary amendment. 16. <input type="checkbox"/> A substitute specification. 17. <input checked="" type="checkbox"/> A change of power of attorney and/or address letter. 18. <input checked="" type="checkbox"/> Certificate of Mailing by Express Mail 19. <input type="checkbox"/> Other items or information: 					
17. General Power of Attorney 18. Express Mailing Label No.: EJ236616789US					

U.S. APPLICATION NO. (IF KNOWN) SEE 37 CFR		INTERNATIONAL APPLICATION NO.		ATTORNEY'S DOCKET NUMBER	
097462971		PCT/US98/15229		AD6516	
20. The following fees are submitted:.				CALCULATIONS PTO USE ONLY	
BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) :					
<input checked="" type="checkbox"/> Search Report has been prepared by the EPO or JPO \$840.00					
<input type="checkbox"/> International preliminary examination fee paid to USPTO (37 CFR 1.482) \$670.00					
<input type="checkbox"/> No international preliminary examination fee paid to USPTO (37 CFR 1.482) but international search fee paid to USPTO (37 CFR 1.445(a)(2)) \$760.00					
<input type="checkbox"/> Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2) paid to USPTO \$970.00					
<input type="checkbox"/> International preliminary examination fee paid to USPTO (37 CFR 1.482) and all claims satisfied provisions of PCT Article 33(2)-(4) \$96.00					
ENTER APPROPRIATE BASIC FEE AMOUNT =				\$840.00	
Surcharge of \$130.00 for furnishing the oath or declaration later than months from the earliest claimed priority date (37 CFR 1.492 (e)). <input type="checkbox"/> 20 <input checked="" type="checkbox"/> 30				\$130.00	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	6 - 20 =	0	x \$18.00	\$0.00	
Independent claims	1 - 3 =	0	x \$78.00	\$0.00	
Multiple Dependent Claims (check if applicable).			<input type="checkbox"/>	\$0.00	
TOTAL OF ABOVE CALCULATIONS =				\$970.00	
Reduction of 1/2 for filing by small entity, if applicable. Verified Small Entity Statement must also be filed (Note 37 CFR 1.9, 1.27, 1.28) (check if applicable).				<input type="checkbox"/>	\$0.00
SUBTOTAL =				\$970.00	
Processing fee of \$130.00 for furnishing the English translation later than months from the earliest claimed priority date (37 CFR 1.492 (f)). <input type="checkbox"/> 20 <input type="checkbox"/> 30				+\$0.00	
TOTAL NATIONAL FEE =				\$970.00	
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable).				<input type="checkbox"/>	\$0.00
TOTAL FEES ENCLOSED =				\$970.00	
				Amount to be: refunded	\$
				charged	\$
<input type="checkbox"/> A check in the amount of to cover the above fees is enclosed.					
<input checked="" type="checkbox"/> Please charge my Deposit Account No. 04-1928 in the amount of \$970.00 to cover the above fees. A duplicate copy of this sheet is enclosed.					
<input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any fees which may be required, or credit any overpayment to Deposit Account No. 04-1928 A duplicate copy of this sheet is enclosed.					
NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.					
SEND ALL CORRESPONDENCE TO:					
KELLY, Patricia L. E.I. DU PONT DE NEMOURS AND COMPANY LEGAL PATENT RECORDS CENTER 1007 MARKET STREET WILMINGTON, DELAWARE 19898 US			SIGNATURE Bart E. Lerman Reg. No. 31,897 for Patricia L. KELLY NAME 39,247 REGISTRATION NUMBER 14 JANUARY 2000 DATE		

TitleFLAME RETARDANT POLYOLEFIN COMPOSITIONS

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Background of the InventionField of Invention:

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This invention relates to polyolefin compositions and more particularly to such compositions which are halogen-free and flame retardant, and to shaped articles made from them.

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Background Discussion:

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Polyvinyl chloride (PVC) products have been on the market for many years and are commonly used in a large variety of applications. With the trend toward a chlorine-free environment, certain market segments such as the construction and wires and cables industries are in need of an alternative to PVC. Several halogen-free flame-retardant compounds are already available on the market but require difficult mixing processes. These compounds often need to be produced by specialized compounders, as the wire and cable and floor tile producers, themselves, often do not have the expertise.

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For wire and cable applications, halogen-free flame-retardant materials are desirable to provide both insulation and jacketing in low-voltage cables in areas where it is necessary to avoid the generation of hazardous gases in the event of fire. Such areas where halogen-free low-voltage cables are useful include hotels, hospitals, schools, theaters and other such public spaces.

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Important characteristics for jacketing materials is that they are highly flame retardant, good heat performance and good physical properties.

- 5 U.S. Patent Nos. 4,948,669, 4,430,468, 4,434,258, 4,673,620, 4,701,359 disclose PVC-free compositions that are suitable for use as coatings for electrical cables. These compositions contain several components that are similar to those described herein, but lack, i.a., the
10 terpolymer described herein.

Summary of the Invention

- According to the present invention there is provided a
15 flame retardant, halogen-free polymer composition comprising a blend of

- (1) ethylene vinyl acetate carbon monoxide terpolymer containing 30-90% by weight ethylene, 10-70% by
20 weight vinyl acetate and 1-40% by weight carbon monoxide;
- (2) an ethylene vinyl acetate or polyolefin selected from the group consisting of (a) ethylene vinyl acetate
25 containing 25-90% by weight ethylene and 10-75% by weight vinyl acetate, (b) a linear low density polyethylene, (c) a low density polyethylene, (d) a very low density polyethylene and (d) a high density polyethylene; and mixtures thereof;
- 30 (3) an ethylene vinyl acetate or polyolefin selected from the group consisting of (a) ethylene vinyl acetate containing 25-90% by weight ethylene and 10-75% by weight vinyl acetate, (b) a linear low density
35 polyethylene, (c) a low density polyethylene, (d) a very low density polyethylene and (d) a high density polyethylene; and mixtures thereof; each of which is grafted with 0.05-3 % by weight of a carboxylic acid or an anhydride thereof; and

(4) an inorganic filler.

Common additives which may be included in the composition of the present invention include antioxidants, titanium dioxide (for UV resistance and to give a white color to the product), processing aids like zinc stearate and UV stabilizers.

10 Detailed Description of the Invention

The present invention relates to flame retardant, halogen-free thermoplastic polymer blends which are useful in wire and cable coatings or in sheet form such as for use in floor tiles. These blends generally are formed by combining an ethylene vinyl acetate carbon monoxide (EVACO) terpolymer, an ethylene vinyl acetate (EVA) copolymer or polyolefin selected from EVA copolymer, a linear low density polyethylene, a low density polyethylene, a very low density polyethylene, a high density polyethylene and mixtures thereof, an ethylene vinyl acetate (EVA) copolymer or polyolefin selected from EVA copolymer, a linear low density polyethylene, a low density polyethylene, a very low density polyethylene, a high density polyethylene and mixtures thereof, each of which is grafted with a carboxylic acid or anhydride thereof, and an inorganic filler.

30 Polymer blends according to the present invention can be formed into wire and cable coatings or sheet form for uses such as for floor tiles, and have many properties comparable to polyvinyl chloride (PVC) containing blends, but are free from halogen.

35 Unless otherwise stated, percentage weight ranges for each of the components in the composition of the present invention are calculated exclusive of any additives which may be present.

The EVACO terpolymer (component (1)) useful in this invention preferably contains 30-90% by weight of ethylene, 10-70% by weight of vinyl acetate and 1-20% by weight of carbon monoxide, more preferably 55-65% by weight of ethylene and 20-30% by weight of vinyl acetate and 5-15% by weight carbon monoxide. In general, these EVACO's have a melt flow index (MFI) in the range of 1-50 g/10 min., preferably in the range of 10-40 g/10min. as determined by ASTM D-1238 (measured at 2,16 kg and 190 °C) and are well-known in the art.

Component (1) preferably comprises 1-60% by weight of the composition of the present invention, more preferably 5-25% by weight, still more preferably 5-15% by weight.

The EVA copolymer when used as component (2) in this invention preferably contains 25-90% by weight of ethylene and 10-75% by weight of vinyl acetate, more preferably 55-75 % by weight of ethylene and 15-30 % by weight of vinyl acetate. In general, these EVA's have a melt flow index (MFI) in the range of 0.05-100 g/10 min., preferably less than 50 g/10min. as determined by ASTM D-1238 (measured at 2,16 kg and 190 °C) and are well-known in the art.

The polyolefins when used as component (2) in general will have a melt flow index (MFI) in the range of 0.05-100 g/10 min., preferably less than 50 g/10min. as determined by ASTM D-1238 (measured at 2,16 kg and 190 °C) and are well-known in the art.

Component (2) preferably comprises 1-50% by weight of the composition of the present invention, more preferably 5-25% by weight, still more preferably 10-20% by weight.

Component (3) is as defined as for component (2), but is further grafted with 0.05-3 % by weight of a carboxylic acid or anhydride thereof, preferably maleic anhydride.

In general, component (3) will have a melt flow index (MFI) in the range of 0.05-100 g/10 min., preferably less than 20 g/10min. as determined by ASTM D-1238 (measured at 2,16 kg and 190 °C).

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Component (3) preferably comprises 1-40% by weight of the composition of the present invention, more preferably 1-15% by weight, still more preferably 3-10% by weight.

- 10 Component (4) is an inorganic filler. Suitable inorganic fillers are known in the art; preferred ones will also possess flame retardant characteristics. Specific, preferred inorganic fillers include aluminum trihydrate, magnesium hydroxide, calcium carbonate, calcinated clay, talcum, mica, zinc borates and mixtures thereof.

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Component (4) preferably comprises 20-85% by weight of the composition of the present invention, more preferably 50-75% by weight, still more preferably 60-70% by weight.

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The grafted moieties of component (3) tend to react with the inorganic filler of component (4) (c.f. K. Hausmann, V. Flaris, Polymers & Polymer Composites Vol. 5, No 2, 1997 p 113 ff. This leads to further compatibilization of the composition. Compositions with higher levels of compatibilization have higher mechanical strength, which allow for higher levels of inorganic filler and thus, compositions with higher flame retardancy.

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- 30 In addition to its polymer and flame retardant filler components, the composition of the present invention can be blended with common additives such as antioxidants, UV stabilizers, lubricants (e.g., oleamide), antiblocking agents, antistatic agents, waxes, pigments, titanium dioxide, talc and other processing aids (e.g., zinc stearate) known in the polymer compounding art. The additives may comprise up to about 10 weight percent of the total composition based on polymer components, flame retardant fillers plus additives.

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The blends of the invention can be prepared by mixing the polymeric ingredients flame retardant fillers and optional additives by use of conventional masticating equipment, for example, a rubber mill, Brabender Mixer, Banbury Mixer, Buss-ko kneader, Farrel continuous mixer or twin screw continuous mixer. Mixing times should be sufficient to obtain homogeneous blends and a proper reaction between maleic anhydride groups and the flame retardant fillers (component (4)). Typically, mixing times of about 5 minutes and mixing temperatures of 160 °C are satisfactory. If the polymer blend is non-homogeneous, additional mixing is required.

The invention can be further understood by the following examples in which parts and percentages are by weight or in parts per hundred rubber (phr) and temperatures are in degrees Celsius.

Examples 1-4

Legend

MFI = melt flow index

EVACO = ethylene vinyl acetate carbon monoxide

EVA = ethylene vinyl acetate

EVA+MAH = ethylene vinyl acetate grafted with maleic anhydride

HDPE+MAH = high density polyethylene grafted with maleic anhydride

ATH = aluminum trihydrate

MAH = maleic anhydride

Procedure

A blend is prepared by melt-compounding the following components in the proportions set forth in Table 1 below.

- EVACO (71.5% ethylene, 20.5% vinyl acetate and 8% carbon monoxide) having a MFI (190°/2.16 kg) of 15
- EVA (72% ethylene and 28% vinyl acetate) having a MFI (190°/2.16 kg) of 3.0
- 5 • EVA+MAH (72% ethylene and 28% vinyl acetate grafted with 1.5 % MAH) having a MFI (190°/2.16 kg) of 1.4
- HDPE+MAH (grafted with 0.9 % MAH) having a density of 0.955 g/cc and a MFI (190°/2.16 kg) of 2.0
- VLDPE having a density of 0.902 g/cc and a MFI
- 10 (190°/2.16 kg) of 1.0
- antioxidant - phenolic type available under the name IRGANOX 1010 from Ciba Specialty Chemicals

Melt compounding is carried out on a two roll mill with

15 batches from 100 grams at 150-170 °C for ca. 5 minutes. The milled product is formed into a testing plaque in a hydraulic press at 150-170 °C for 5 minutes. Afterwards stress-strain testing (ASTM D-412), Limited Oxygen Index i.e. LOI (ASTM D 2863) and Knife Penetration at 80 and 90

20 °C (IEC 540 Item 10.1) are carried out. Results are shown in Table 1.

T a b l e 1

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<u>Example numbers</u>	<u>1</u>	<u>2</u>
EVACO	10	10
EVA	16	13
30 EVA+MAH	9	4
HDPE+MAH	-	4
VLDPE	-	4
ATH	64.7	64.7
Antioxidant	0.3	0.3
35 Tensile strength (MPa)	14.6	15.7
Tensile elongation (%)	150	140
Knife Penetr. at 80 °C (%)	80	0
Knife Penetr. at 90 °C (%)	100	0
LOI (%)	38	35

One can see that the formulation containing HDPE+MAH and VLDPE show particularly lower knife penetration values (better heat performance) but lower flame retardancy than the formulation without. For some wire and cable applications, heat performance can be of major importance while in others flame retardancy is the most important criteria .

Claims

1. A flame retardant, halogen-free polymer composition comprising a blend of

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- (1) ethylene vinyl acetate carbon monoxide terpolymer containing 30-90% by weight ethylene, 10-70% by weight vinyl acetate and 1-40% by weight carbon monoxide;

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- (2) an ethylene vinyl acetate or polyolefin selected from the group consisting of (a) ethylene vinyl acetate containing 25-90% by weight ethylene and 10-75% by weight vinyl acetate, (b) a linear low density polyethylene, (c) a low density polyethylene, (d) a very low density polyethylene and (d) a high density polyethylene; and mixtures thereof;

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- (3) an ethylene vinyl acetate or polyolefin selected from the group consisting of (a) ethylene vinyl acetate containing 25-90% by weight ethylene and 10-75% by weight vinyl acetate, (b) a linear low density polyethylene, (c) a low density polyethylene, (d) a very low density polyethylene and (d) a high density polyethylene; and mixtures thereof; each of which is grafted with 0.05-3 % by weight of a carboxylic acid or an anhydride thereof; and

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- (4) an inorganic filler.

2. A blend according to claim 1 wherein component (1) comprises 1-60 % by weight of the blend, component (2) comprises 1-50 % by weight of the blend, component (3) comprises 1-40 % by weight of the blend, and component (4) comprises 20-85% by weight of the blend.

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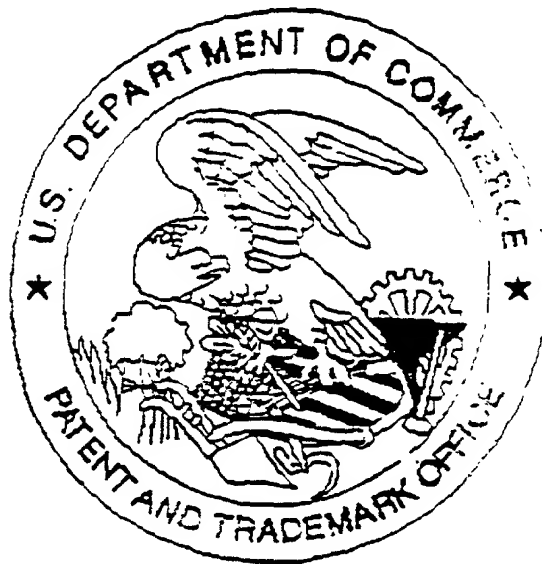
3. A blend according to claim 1 wherein component (1) comprises 5-25% by weight of the blend, component (2) comprises 5-25% by weight of the blend component (3) comprises 1-15% by weight of the blend, and component
5 (4) comprises 50-75% by weight of the blend.
4. A blend according to claim 1 wherein component (1) comprises 5-15% by weight of the blend, component (2) comprises 10-20% by weight of the blend component (3)
10 comprises 3-10% by weight of the blend, and component (4) comprises 60-70% by weight of the blend.
5. A blend according to claim 1 wherein component (4) is
15 aluminum trihydrate, magnesium hydroxide, calcium carbonate, calcinated clay, talcum, ammonium polyphosphate or a mixture thereof
6. A shaped article formed from a blend according to claim 1.

DECLARATION and POWER OF ATTORNEY

As a below-named inventor, I hereby declare that: My residence, post office address and citizenship are as stated below next to my name. I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled: FLAME RETARDANT POLYOLEFIN COMPOSITIONS the specification of which is attached hereto unless the following box is checked: <input checked="" type="checkbox"/> was filed on 23 JULY 1998 as U.S. Application No. _____ or PCT International Application No. PCT/US98/15229 and was amended on _____ (if applicable).			
I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above. I acknowledge the duty to disclose information which is known to me to be material to patentability as defined in 37 CFR § 1.56. I hereby claim foreign priority benefits under 35 U.S.C. § 119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed.			
Application No. 97202335.2	Country EP	Filing Date 25 JULY 1997	Priority Claimed (Yes/No) Yes
I hereby claim the benefit under 35 U.S.C. § 119(e) of any United States Provisional Application(s) listed below. U.S. Provisional Application No. _____ U.S. Filing Date _____			
I hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s), or § 365(c) of any PCT International Application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States application or PCT International Application in the manner provided by the first paragraph of 35 U.S.C. § 112, I acknowledge the duty to disclose information which is known to me to be material to patentability as defined in 37 CFR § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.			
Application No.	Filing Date	Status (patented, pending or abandoned)	
POWER OF ATTORNEY: I hereby appoint the following attorney(s) and/or agent(s) the power to prosecute this application and transact all business in the Patent and Trademark Office connected therewith:			
Name: PATRICIA L. KELLY		Registration No.: 39,247	
Send correspondence and direct telephone calls to: PATRICIA L. KELLY		E. I. du Pont de Nemours and Company Legal - Patents Wilmington, DE 19898, U.S.A. Tel. No. (302) 992-6743 Fax No. (302) 992-2953	
I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.			
INVENTOR(S)			
Full Name of Inventor	Last Name GARCIA DURAN	First Name JUAN	Middle Name ANTONIO
	Signature (please sign full name): <i>Juan Antonio Garcia</i>		Date: 20.06.2000
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			Zip Code CH-1208
Full Name of Inventor	Last Name ROLLAND	First Name LOIC	Middle Name PIERRE
	Signature (please sign full name): <i>Loic Rolland</i>		Date: June 15, 2000
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			Zip Code F-01220

☐ Additional Inventors are being named on separately numbered sheets attached hereto.

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